Magnetron Sputtered $Ba_{(1-x)}Sr_xTiO_3$ Thin Films

E. J. Cukauskas, S. W. Kirchoefer, and J. M. Pond
Naval Research Laboratory, Washington, DC, USA

Abstract — Thin films of $Ba_{(1-x)}Sr_xTiO_3$ (BST) have been deposited by Inverted Cylindrical Magnetron (ICM) and off-axis cosputtering at high sputter gas pressures. The ICM technique uses a single BST target and the off-axis technique uses $BaTiO_3$ and $SrTiO_3$ targets. Films were deposited at gas pressures ranging from 6.7 to 53 Pa and at substrate temperatures from 550 to 800°C. By combining high gas pressures with unconventional geometries the negative ion bombardment of the growing film, characteristic of oxide film growth, has been minimized. This results in well oxygenated stoichiometric BST films. The surface morphology and grain structure were investigated and related to the measured microwave properties. The films had lattice parameters dependent on deposition conditions. Grain sizes were approximately 0.25 µm for most films after an oxygen anneal at 780° C. Both techniques have yielded films having Q > 1000 with tuning of nearly 7%.

Introduction

Thin film $Ba_{(1-x)}Sr_xTiO_3$ (BST) is a perovskite ferroelectric having applications in room temperature tuneable microwave components and in Dynamic Random Access Memory (DRAM) for computer memory elements [1, 2]. Of particular technological importance for BST is the relationships between its dielectric properties, morphology, and composition. BST forms a solid solution for all Ba/Sr metals fractions, allowing for tailoring the dielectric characteristics for room temperature applications. Dielectric tuning and loss are two inter-related properties dependent on the Curie temperature and operating temperature. The Curie temperature is known to depend on the unit cell volume regardless of the source of lattice parameter distortion [3]. These changes in the lattice parameter are related to grain morphology and can result from film stress, grain size, grain orientation, oxygen vacancies, cation off stoichiometry, impurity doping, and other morphological defects. Many of these film defects are very dependent on the deposition parameters and technique used for film growth. Sputtering is one of several growth techniques suitable for wafer scale processing.

Conventional parallel plate rf sputtering of BST thin films is very susceptible to back sputtering the growing film by negative oxygen ions. This can lead to off-stoichiometric films having inferior dielectric properties and leakage currents. These adverse effects can be minimized by using a composition compensated target, high sputtering gas pressure, or an unconventional growth geometry [4, 5]. We report results on the growth of thin film BST deposited by the unconventional techniques of off-axis cosputtering $BaTiO_3$ (BTO) and $SrTiO_3$ (STO) and by the technique of Inverted Cylindrical Magnetron (ICM) sputtering. The dielectric properties are related to the deposition parameters and film morphology.

Experimental Details

BST thin films were off-axis cosputtered onto (100) MgO and (100) $LaAlO_3$ substrates held at a temperature of 550°C in a 3/1 Ar/O_2 gas mixture. The gas pressure was 20 Pa (150 µm). The film composition was set by the relative rf power levels supplied to each magnetron sputter gun. The facing targets geometry supports the reaction of the BTO and STO sputtered species in the plasma, at opposing target surfaces, and on the substrate surface [6]. A post oxygen anneal at 780° C for 8 hours was done to insure complete reaction in the event a fine grained BTO/STO composite was formed. The anneal further insures complete oxygenation of the resultant BST film. Because of its relatively low deposition rate (< 1 kÅ/h), the off-axis cosputtering technique is particularly useful for parallel plate capacitor applications.

The ICM sputtering technique was also used to deposit BST thin films. Deposition rates of 2 - 3 kÅ/h are achievable with ICM sputtering [5]. BST thin films were ICM sputtered at a substrate temperature of 750° C in a 85% O_2/Ar gas mixture. A gas pressure of 53 Pa (400 µm) was used for the ICM sputtered films unless otherwise stated. A hollow cylindrical $Ba_{0.5}Sr_{0.5}TiO_3$ composite target of 99.9% purity was used for film growth. The ICM sputtered films were also post annealed in oxygen at 780° C for 8 hours.

The film morphology was investigated by x-ray diffractometry and Atomic Force Microscopy (AFM). The films were then processed into interdigitated capacitors for dielectric characterization at frequencies to 20 GHz.

Structural Characterization

The crystallite structure of the BST thin films was determined from scans taken on a Phillips automated independent theta-two-theta diffractometer. All films x-rayed showed the BST structure with no sign of BTO or STO diffraction peaks. X-ray scans were taken in two-theta from 20 to as high as 110 degrees for some films. The two-theta peak positions were analyzed using the

Nelson-Riley error correction and a least squares fit [7, 8]. In general the off-axis cosputtered films were multi-textured with the (h00) diffraction lines dominating the spectrum. In changing the relative BTO and STO gun rf power levels such that the film has a higher Sr ($x > 0.5$) composition, the preferred orientation becomes purely (h00). The orientation becomes predominantly (110) and (111) for films having a greater Ba ($x < 0.5$) composition. Fig. 1 illustrates the x-ray scan for an off-axis cosputtered $Ba_{0.6}Sr_{0.4}TiO_3$ film having a predominantly (110) orientation. The MgO substrate peak around 43 degrees has been suppressed for clarity.

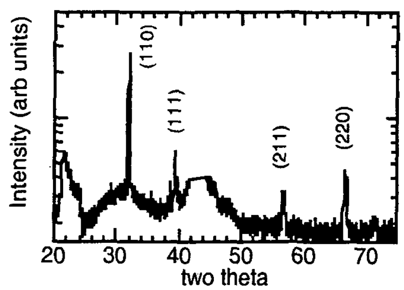

Fig. 1 The x-ray scan for an off-axis cosputtered Ba-rich BST film showing a (110) preferred crystallite orientation.

The BST films deposited by the ICM sputtering technique were predominantly (h00) oriented for the set of sputtering parameters listed above. The film orientation was dependent on the parameters of substrate temperature, substrate to target spacing, gas composition, and gas pressure. Multi-textured and (110) oriented ICM sputtered films were deposited under different conditions. The detailed morphology and its relation to other film properties will be reported elsewhere. The x-ray scan for an ICM sputtered film deposited at a substrate temperature of 750° C, 53 Pa gas pressure, and 85% oxygen is illustrated in Fig. 2. The film is strongly (h00)

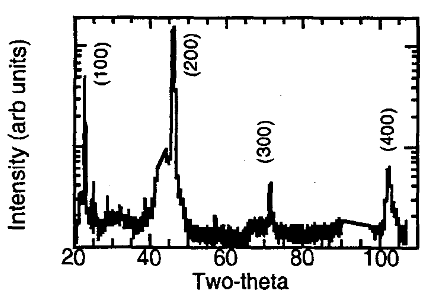

Fig. 2 The x-ray scan for an ICM sputtered film showing strong (h00) orientation.

oriented, however there are weak peaks at the (110), (111), and (211) positions. The MgO substrate peaks were suppressed from the data trace. We found that the film structural characteristics were near optimum for a O_2/Ar gas composition consisting of 85% oxygen. BST films made with less than 5% O_2 did not show the BST structure. Films were made with 100% O_2 and had similar x-ray scans as in Fig. 2 with slightly lower peak intensities.

Surface Morphology

The surface morphology of the BST films was investigated using a Digital Instruments model IIIa Atomic Force Microscope (AFM). The off-axis cosputtered films deposited at 550° C were specular to the eye, however the ICM films deposited at 750° C were visually rough. The surface roughness was measured for the off-axis and ICM sputtered BST films and was found to be related to the crystallite orientation. The visually smooth cosputtered films had orientations of (110) and (111) grains while the rough ICM films were strongly (h00) oriented. Even those films which were specular to the eye showed the orientation dependence of the roughness. Fig. 3 illustrates an AFM image of the surface of an ICM sputtered BST film having a rms surface roughness equal to 15.7 Å.

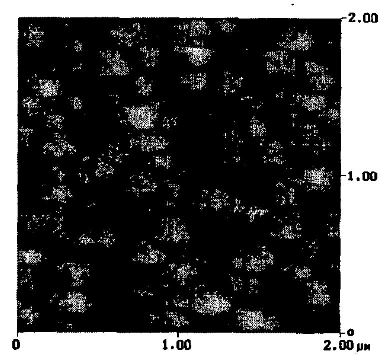

Fig. 3 The surface micrograph of an ICM sputtered film at 750° C at 20 Pa gas pressure.

The surface roughness was found to be dependent on the substrate temperature and sputter gas pressure. A reduced sputter gas pressure resulted in smoother films even at the high substrate temperatures. The low gas pressure also increased the deposition rate. The film surface illustrated in Fig. 3 for a film deposited at a gas pressure of 20 Pa was found to have a roughness nearly 1/3 that of films made at same temperature and at 53 Pa pressure. The pressure and temperature dependence of the surface roughness is related to the in plane and c-axis growth rates, where the c-axis is taken to be perpendicular to the substrate. An oblique view of the film surface showed the c-axis grains as spikes protruding above a background continuous film. The spikes consist of numerous smaller grains tightly coupled forming the larger grain structure. This protruding grain structure results from a higher growth rate along the c-axis which is accelerated in relation to the in-plane growth rate at higher temperatures and pressures. The grain size is estimated to be approximately 0.25 μm from Fig. 3. The grain size is the same for the off-axis sputtered films and is determined predominantly by the post annealing conditions.

Characterization and Discussion

The BST films were processed into interdigitated capacitors, mounted on a microwave probe station, and characterized using a HP8510C vector network analyzer. Reflection measurements (S_{11}) were made from 50 MHz to 20 GHz under bias voltages from -40 V to +40 V in 5 V increments. A parallel resistor-capacitor circuit model was used to analyze the data and extract the relative dielectric constant [9, 10]. The capacitive tuning in % was calculated by the relation, 100 x (C(0) - C(40))/C(0), where C(0) and C(40) are the capacitance at zero and 40 Volts bias, respectively. The average Q was calculated from the values at zero and 40 Volts. These results, measured at 10 GHz and other film properties are tabulated for a number of representative films in Table I.

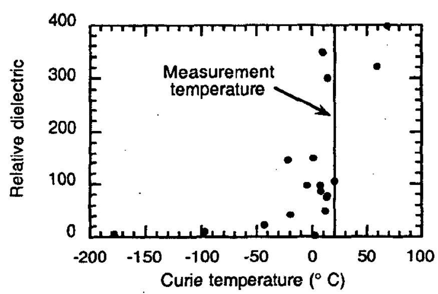

Fig. 4 The relative dielectric constant as a function of the Curie temperature for a number of BST films having the same composition.

Inspection of Table I shows a range of dielectric properties for films having the same BST composition. These variations resulted after changes in the deposition parameters and suggest there may be a dependence on the initial grain morphology associated with the film growth process. The Curie temperature (T_c) was determined from the lattice parameter for films deposited by both deposition techniques. The dielectric constant was also determined for a variety of films deposited under various conditions, however all films had the same BST composition. Illustrated in Fig. 4 is the relative dielectric constant plotted as a function of the Curie temperature as determined from the measured lattice parameter. The measurement temperature is indicated by the vertical line as a temperature reference.

As the value of T_c becomes closer to the measurement temperature, the relative dielectric constant increases in magnitude as expected. Those films having T_c below the measurement temperature are in the paraelectric state and have the highest Q values (lowest loss). Films having T_c above the measurement temperature are in the ferroelectric state and have lower Q values. There is an apparent trade-off between Q and tuning for BST thin films. The Figure - Of - Merit (FOM) listed in Table I is the product of the fractional tuning and average Q (Q_{av}). This allows for film - to - film comparison. The tuning characteristics of the capacitors had the same dependence on T_c as the relative dielectric constant. Fig. 4 indicates that the Curie temperature should be relatively close to the operating temperature for the greatest tuning and relative dielectric.

Capacitance vs. voltage measurements made on the devices showed various degrees of hysteresis depending on the Curie temperature. The largest hysteresis was observed for those devices where the Curie temperature was close to the 20° C measurement temperature. The degree of hysteresis rapidly decreased as the difference between T_c and the measurement temperature became large. Those devices which were far into the paraelectric state showed very little hysteresis. Fig. 5 illustrates the relative dielectric constant versus voltage for a device having a T_c = 11.5° C. The measurement frequency was 10 GHz. Based on its T_c, this device is in the paraelectric state. However, the hysteresis for this device results from a range in film Curie temperatures.

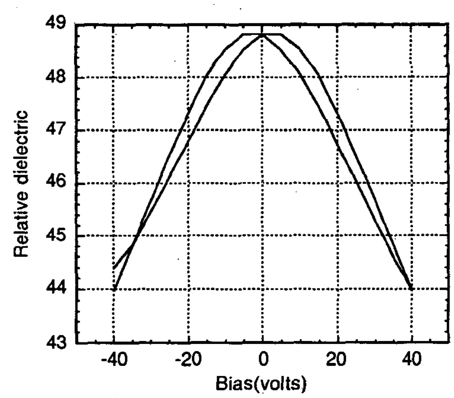

Fig. 5 The relative dielectric constant as a function of bias voltage measured at 10 GHz. T_c was 11.5 °C.

Hysteresis is dependent on the grain structure through its relationship with the Curie temperature. The grain structure illustrated in Fig. 3 above shows that the grains form clusters of smaller grains. In some of these clusters, the grain boundaries are barely discernible. This grain structure gives rise to a non-uniform intergranular stress resulting in a range of Curie temperatures within the film. This film stress shows up as a distortion of the cubic BST unit cell structure. Most of the BST films show a small tetragonal distortion to the cubic structure which we associate with the intergranular stress. The degree of this distortion and an enlargement of the unit cell volume can be further enhanced by oxygen vacancies [3].

Table I: The dielectric characteristics and material properties of selected BST thin films

Technique	a_0(Å)	T_c(° C)	ε	Tuning (%)	Q_{av}	FOM	Remarks
off-axis	3.9772	59.35	322	13.5	39	5.27	(110)
off-axis	3.9530	-21.59	146	4.9	250	12.33	
off-axis	3.9623	9.52	349	13.8	65	8.97	$LaAlO_3$
off-axis	3.9800	68.7	398	25.2	26.5	6.68	seed layer
ICM	3.9580	-4.87	97	5.6	156	8.74	
ICM	3.9466	-43	22.8	1.0	>1000	>10	
ICM	3.9629	11.52	49	4.39	55	2.42	hysteresis

Summary and Conclusions

We have investigated the properties of BST thin films deposited by unconventional sputtering techniques. The films were deposited by off-axis cosputtering of BTO and STO targets and by inverted cylindrical magnetron sputtering. Stoichiometric films are realized from these techniques because of their geometry and high sputter gas pressures. Thin film BST was deposited having very low dielectric loss, beyond the resolution of the measurement technique. Additionally, tuning as great as 30 % was achieved for some films. However, there was a trade-off between tuning and loss. Films having the lowest loss tended to have small tuning.

The film morphology was strongly dependent on the deposition conditions. BST films were deposited having purely (h00) or (110) and (111) preferred orientation from both growth techniques. The surface roughness was observed to increase with substrate temperature and sputter gas pressure. AFM measurements revealed a growth rate anisotropy with the growth rate along the (h00) direction much greater than in the substrate plane. The small (~ 0.25 μm) grain size contributed to low loss properties and small tuning in the films.

The Curie temperature was determined from its dependence on the unit cell volume. Examination of the dielectric properties in relation to the Curie temperature revealed that most of the films were in the paraelectric state. Changes in the growth parameters resulted in changes in the Curie temperature for films having the same composition. The voltage dependence of the relative dielectric showed hysteresis for those films close to the Curie temperature. The hysteresis sharply decreased as the difference between the Curie temperature and measurement temperature became large. These results are consistent with fined grained BST having a distribution of Curie temperatures. Furthermore, the importance of the initial growth layers in relation to optimum operating temperatures needs continued study.

These films show promise for applications in low loss microwave circuits and computer memory elements.

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